

US EPA ARCHIVE DOCUMENT

APPENDIX G – ATTACHMENT 3

Bioaccumulation Data Evaluation

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Bioaccumulation Data Evaluation

Summary

Composite samples of muscle tissue of three fish species taken annually by hook-and-line fishing near the Honouliuli outfall diffuser for the period 1991 through 1995 were analyzed annually to determine the body-burden of priority pollutants in muscle tissue. Liver tissues were not analyzed because they were not "edible" tissues normally consumed by humans.

Whole fish were sampled in the field and frozen for shipment to the analytical laboratory for resection and composting of muscle tissue. Sample sizes ranged from 7 to 14 fish per composite. Results to date reveal few samples with detectable concentrations of volatile and base neutral organic compounds. Selected trace metals and a few chlorinated organic compounds (pesticide residues including p,p'DDT, p,p'DDE, Endosulfan and the PCB Arochlors 1254 and 1260) were present in muscle tissue samples at low concentrations when detectable.

In all but a few cases, the concentrations of metals in the tissues of fish from the city's study area are consistent with concentrations from other areas of the Hawaiian Islands, including areas considered to be removed from the immediate influences of contaminant input sources (City & County of Honolulu, 1994).

A complicating factor in interpreting the data is proximity of some of the sampling sites to Pearl Harbor, which is known to have relatively high levels of selected contaminants compared to other areas of Mamala Bay (M&E Pacific, 1989). The only possible exceptions, to what appear to be normal tissue burdens are concentrations of arsenic, which is found in relatively high concentrations. Other trace metals show no evidence of bioaccumulation of metals in the fish tissues. There do not appear to be species-specific differences in the concentrations of contaminants. If there are differences they could be reflective of diet or physiology or residency near known sources of contaminants (such as Pearl Harbor or the outfall diffuser).

The overall concentrations of trace metals found in rig-caught fish caught near the Honouliuli outfall are consistent with findings from other outfall bioaccumulation studies done along the Pacific coast (e.g., Young and Moore, 1978; Brown, 1986; Mearns et al., 1991; and Spies, 1984), which indicate that trace metals, with the possible exception of mercury and arsenic, do not accumulate in the tissues of fish. Most fish have the ability to detoxify and eliminate excess metals from their system (e.g., Brown et al., 1982).

Mean muscle tissue mercury levels have not exceeded the U.S. Food and Drug Administration Action Levels or the Hawaii Department of Health advisory levels for any constituents.

Introduction

Bioaccumulation is the general term describing a process by which chemicals are taken up by marine organisms from water directly or through consumption of food containing the chemicals (Rand and Petrocelli, 1985). EPA's 301(h) program guidelines define bioaccumulation as the process of biological uptake and retention of chemical contaminants derived from various exposure pathways (Tetra Tech 1985).

Methods

Annually, the city laboratory ocean monitoring crew conducts hook-and-line fishing near the outfall diffuser to collect fish for analysis to determine body burdens of various contaminants.

Data on fish size class and standard length, and biomass are recorded on several field data sheets and presented with the analytical information. Additional details are presented in the city's Annual Assessment Reports (City & County of Honolulu, 1991, 1992, 1993 and 1994).

Hook-and-Line Fishing Surveys

Various fish species which are commonly caught and eaten by local recreational and commercial fishermen are sampled using baited hooks at a single locality (near the outfall diffuser), which is assumed to represent a "worst-case" situation with regard to possible exposure and uptake of potential pollutants that might be present in the wastewater effluent.

Fish are caught by hook and line by city staff using long-line rigs consisting of 100-meter sections of 1/4-inch twisted nylon line with anchors at either end. A line and surface buoy are attached to one of the anchors for retrieving the rig after it is fished. The nylon line is marked at 2-meter intervals for hook and leader attachment and has seven evenly spaced marks along its length as site for attaching small subsurface floats used to prevent entanglement on reefs and debris. Fresh or frozen anchovies, mackerel and frozen squid are used for bait, and attempts are made to alternate the various baits and hook sizes in a random manner in order to catch fish of various sizes and species. The catch is weighed, tagged, and the data recorded on data sheets prior to being wrapped in aluminum foil and put into Ziplock plastic bags. It is then put on dry ice for transport to the laboratory freezer. Dissected muscle samples are obtained from the fish in the laboratory after they are shipped and thawed for analysis.

Three replicate composite samples are taken from a pool of several individuals of each target species. The composite muscle samples are analyzed for tissue burden levels of priority pollutants, trace metals, chlorinated pesticides and PCBs, and volatile and semivolatile organic compounds using EPA methods. The results obtained from the composite samples each year for each species for detectable priority pollutants (including a few common laboratory contaminants) are summarized in Tables G-3-2 through G-3-5 for the three species of fish.

Assessment Methodology

Bioaccumulation can be assessed either by inference and known uptake rates or by evaluating the concentrations of various priority pollutants found in the effluent, marine sediments and the tissues of various organisms. The latter approach is that being used in this application. The fish samples were collected by the staff of the City & County of Honolulu's Ocean Monitoring Program, and the analyses were completed by a contract laboratory, PACE Analytical Laboratories, or done in-house. The bioaccumulation issue is assessed using fish caught by hook-and-line (referred to as rig-caught) from the vicinity of the outfall diffuser.

The species caught and subsequently included in the data base (after the screening process) are summarized in Table G-3-1. Both the common and scientific names are shown. For most of the discussions which follow, the common names will be used.

Table G-3-1. Scientific and Common Names of Fish Analyzed as Part of the City & County of Honolulu Honouliuli Outfall Ocean Monitoring Program

<u>Hawaiian/Common Name</u>	<u>Scientific Name</u>	<u>Family</u>
Menpachi (brick soldierfish)	<i>Myripristic cheryseres</i>	Holocentridae
Akule (big-eyed scad)	<i>Trachiurops crumenophthalmus</i>	Carangidae
Ta'ape (blue-lined snapper)	<i>Lutjanus kasmira</i>	Lutjanidae

The bioaccumulation studies were initiated as part of ocean monitoring studies when the present permit became effective. The fish were collected by the city monitoring program crew, and samples were obtained, packaged, frozen and shipped to a contract analytical firm for most analyses. Certain analyses were done by the city laboratory (cyanide). The data were reported back to the city, and analyzed and summarized in the annual assessment reports.

No screening of the data was done as is the case where there are large numbers of samples. Also, most of the organic compounds were nondetectable, and only a few of the metals are routinely measured above detection levels.

Results

The primary focus of this review is to summarize priority pollutant bioaccumulation data collected by the city monitoring program and discuss the findings. All the analyses completed to date were originally reported as $\mu\text{g}/\text{kg}$ (ppb) on a wet weight basis. These were converted to mg/kg (ppm) and will be reported hereinafter and expressed as parts per million (ppm).

Each individual chemical is discussed, starting with mercury and arsenic, two metallic compounds which have been shown to be bioaccumulated in fish throughout the world. High levels of these two metals have been measured in areas remote from wastewater

discharges and other human activities which might contribute to degradation of local water quality (Mearns et al., 1992). Thus, the presence of high concentrations in fish does not necessarily indicate that there is an association with wastewater discharge.

A summary of results for the three target species is presented in Tables G-3-2 through G-3-4.

Table G-3-2. Summary of Bioaccumulation Analyses of Composite Samples of Menpachi Honouliuli Outfall Diffuser

<u>Menpachi Golden-finned squirrelfish</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>5 Year</u>
Analyte conc. mg/kg wet wt	1991	1992	1993	1994	1995	Mean
Arsenic	5.9	11.8	8.1	8.74	15.5	10.01
Cadmium	BDL	BDL	ND	ND<0.050	0.05<0.50	0.00
Chromium	BDL	BDL	0.07	ND<0.20	0.1	0.03
Copper	0.18	0.10	ND	0.2	0.7	0.22
Lead				ND<0.01	ND<0.1	0.00
Mercury	0.13	0.08	0.026	0.059	0.11	0.08
Nickel	BDL	BDL	BDL	ND<0.5	0.2	0.04
Selenium	0.41	BDL	BDL	0.421	0.4	0.25
Silver		<2.99	0.05	0.034	ND<0.02	0.02
Zinc	2.75	2.25	2.1	3.2	2.8	2.62
Heptachlor epoxide	BDL	BDL	BDL	BDL	BDL	0.00
Chlordane, alpha	0.002	BDL	BDL	BDL	BDL	0.00
Dieldrin	0.001	BDL	BDL	BDL	BDL	0.00
4,4-DDE	0.005	BDL	BDL	BDL	BDL	0.00
4,4-DDD	0.013	BDL	BDL	BDL	BDL	0.00
Cyanide	<0.5	<0.5	<0.5	<0.5	<0.5	0.00
Methylene chloride	0.028	BDL	BDL	BDL	BDL	0.01
Di-n-butyl phthalate	BDL	BDL	BDL	BDL	BDL	0.00
bis (2-ethylhexyl) phthalate	2.2	0.17	BDL	BDL	BDL	0.47
Methoxychlor	BDL	0.005	BDL	BDL	BDL	0.00
Chloromethane	ND	ND	ND	0.11	BDL	0.02

Table G-3-3 (Continued)

<u>Menpachi Golden-finned squirrelfish</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>5 Year</u>
Analyte conc. mg/kg wet wt	1991	1992	1993	1994	1995	Mean
Number of fish composited	13	7	13	8	11	10
Average weight, g	166.41	163.44	133.68	93.68	144.60	140.36
Average length, cm	20.69	20.14	18.92	16.88	19.86	19.30

< = Less than
BDL = Below detection limit
ND = Not detected.

**Table G-3-3. Summary of Bioaccumulation Analyses in
Ta'ape Composite Muscles Samples
Honouliuli Outfall Diffuser**

<u>Ta'ape Blue-lined snapper</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>5 Year</u>
<u>Analyte conc. mg/kg wet wt</u>	<u>1991</u>	<u>1992</u>	<u>1993</u>	<u>1994</u>	<u>1995</u>	<u>Mean</u>
Arsenic	3.3	4.49	1.1	5.96	8.1	4.59
Cadmium	BDL	BDL	ND	ND<0.05	ND<0.05	0.00
Chromium	BDL	BDL	0.09	ND<0.20	0.1	0.04
Copper	0.25	0.37	ND	0.3	0.3	0.24
Lead	BDL	BDL	BDL	ND<0.10	ND<0.10	0.00
Mercury	0.06	0.02	0.008	0.078	0.16	0.07
Nickel	BDL	BDL	BDL	ND<0.5	ND<0.5	0.00
Selenium	0.47	BDL	BDL	0.285	0.6	0.27
Silver	BDL	<3.38	BDL	0.042	ND<0.02	0.01
Zinc	2.31	3.66	2.3	2.4	3.4	2.81
Heptachlor epoxide	0.002	NR	BDL	BDL	BDL	0.00
Chlordane, alpha	0.002	NR	BDL	BDL	BDL	0.00
Dieldrin	0.002	NR	BDL	BDL	BDL	0.00
4,4-DDE	0.005	NR	BDL	BDL	BDL	0.00
4,4-DDD	0.004	NR	BDL	BDL	BDL	0.00
Cyanide	<0.5	<0.5	<0.5	<0.5	<0.5	0.00
Methylene chloride	0.094	0.27	BDL	BDL	BDL	0.07
Di-n-butyl phthalate	1.4	NR	BDL	BDL	BDL	0.28
bis (2-Ethylhexyl) phthalate	BDL		BDL	BDL	BDL	0.00
Methoxychlor	BDL		BDL	BDL	BDL	0.00
Number of fish composited	11	11	13	13	12	12.00
Average weight, g	160.64	171.79	205.05	147.88	283.51	193.77
Average length, cm	21.36	21.82	22.92	20.69	26.21	22.60

< = Less than
BDL = Below detection limit
ND = Not detected
NR = No reading

Table G-3-4 (Continued)

Table G-3-4. Summary of Bioaccumulation Analyses in Akule Composite Muscles Samples Honouliuli Outfall Diffuser

<u>Akule</u> <u>Big-Eyed Scad Fish</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>Year</u>	<u>5 Year</u>
Analyte conc. mg/kg wet wt	1991	1992	1993	1994	1995	Mean
Arsenic	1.68	5.07	8.1	3.74	0.40	3.80
Cadmium	ND	ND	0.004	ND<0.05	ND<0.05	0.00
Chromium	ND	0.02	0.09	ND<0.2	0.1	0.04
Copper	0.29	0.13	1.2	0.2	0.65	0.49
Lead	ND	ND	ND	ND	ND<0.1	0.00
Mercury	0.09	0.1	0.034	1.28	0.45	0.39
Nickel	0.06	BDL	BDL	ND<0.5	<0.20	0.01
Selenium	BDL	BDL	BDL	0.45	0.60	0.21
Silver	BDL	<2.84	0.04	ND<0.200	<0.20	0.01
Zinc	3.67	2.03	5.8	1.7	0.495	2.74
Heptachlor epoxide	BDL	ND	BDL	BDL	BDL	0.00
Chlordane, alpha	BDL	BDL	BDL	BDL	BDL	0.00
Dieldrin	BDL	BDL	BDL	BDL	BDL	0.00
4,4-DDE	0.001	BDL	BDL	BDL	BDL	0.00
4,4-DDD	BDL	BDL	BDL	BDL	BDL	0.00
Cyanide	<0.5	<0.5	<0.5	<0.5	<0.5	0.00
Methylene chloride	0.016	BDL	BDL	BDL	BDL	0.00
Di-n-butylphthalate	0.34	BDL	BDL	BDL	BDL	0.07
bis (2-ethylhexyl) phthalate	0.34	0.12	BDL	BDL	BDL	0.09
Methoxychlor	BDL	BDL	BDL	BDL	BDL	0.00
Toluene	BDL	BDL	BDL	BDL	0.00115	0.00
Number of fish composited	12	11	10	14	13	12
Average weight, g	249.28	101.32	264.41	330.79	185.77	226.31
Average length, cm	27.00	21.18	27.40	24.23	23.19	24.60

< = Less than
 BDL = Below detection limit
 ND = Not detected

Mercury

Mercury is a potential contaminant that undergoes bioaccumulation and bioconcentration in the marine food web and can result in adverse human health effects (Montague and Montague, 1971). The degree to which mercury poses a potential health threat to humans has been linked with the degree to which it becomes organically bound (methylated) under certain environmental conditions (anaerobic conditions in sediments). Mercury is not found in found in relatively high concentrations in the Hawaiian environment because there are no geologic formations (cinnabar deposits) such as found in the coastal strata of California.

Honouliuli effluent concentrations are very low and are not recorded at levels above that of the analytical methods used. Concentrations range from <0.4 to <1.0 $\mu\text{g/l}$ (ppb). Mercury concentrations in sediments are also low and have ranged from <0.008 to 0.1667 mg/kg (dry weight basis). The distribution pattern shown through monitoring indicates extremely wide-ranging fluctuations in sediment concentrations both spatially and temporally.

Levels of mercury in sediments near the Honouliuli outfall have been consistently low. (See Attachment C-3 of Appendix C for details.) There has been no pattern of mercury concentrations that can be related to ocean discharge practices from the Honouliuli outfall.

Levels of mercury in the muscle tissue of various fish caught off Barbers Point ranged from 0.026 - 0.13 ppm in menpachi, 0.008 - 0.16 ppm in ta'ape, and 0.034 - 1.28 ppm in akule (Table G-3-4). Ta'ape caught near the Sand Island outfall diffuser had mercury levels in muscle ranging from 0.082 to 0.37 ppm, higher than the levels near Barbers Point. Akule samples for Sand Island ranged from 0.022 to 0.870 ppm slightly lower than the range found at Barbers Point. These ranges are typical of fish caught worldwide (Table G-3-5).

Table G-3-5. Chemical Residues Reported in Marine Fish Worldwide in 1994

<u>Chemical</u>	<u>Concentration ppm, wet wt. (unless otherwise indicated)</u>	<u>Location</u>	<u>Reference</u>
Arsenic	0.016-32.3	Saudi Arabia	Atlar et al., 1992
	0.4-2.1	Pakistan	Tariq et al., 1991
Cadmium	0.2-0.27	Denmark	Jorgensen and Pedersen, 1994
	0.23-1.04	Pakistan	Tariq et al., 1991
	0.03 - 0.2	Turkey	Kucuksezgin and Balci, 1994
	0.01-0.5 (dry wt)	Spain	Pastor et al., 1994
Chromium	1.5-5.1	Turkey	Kucuksezgin and Balci, 1994
	3.3-6.2	Pakistan	Tariq et al., 1991
Copper	0.84-4.8 (dry)	Taiwan	Han et al., 1994
	0.8-2.1	Pakistan	Tariq et al., 1991
	2-18	Denmark	Jorgensen and Pedersen, 1994
Lead	0.3-0.8	Denmark	Jorgensen and Pedersen, 1994
	0.9-2.2	Turkey	Kucuksezgin and Balci, 1994
	0.05-11.2	Spain	Pastor et al., 1994
Mercury	0.03-0.26	Denmark	Jorgensen and Pedersen, 1994
	0.01-0.3	Turkey	Kucuksezgin and Balci, 1994
	0.03-1.4	Spain	Pastor et al., 1994
	0.08-1.02	Israel	Hornung et al., 1994
	0.003-0.16	Pakistan	Tariq et al., 1991
	0.13-3.2	Italy	Barghigiani and deRamién, 1992.
Nickel	0.77-3.25	Pakistan	Tariq et al., 1991
Silver	0.2-1.76	Pakistan	Tariq et al., 1991

Table G-3-6 (Continued)

<u>Chemical</u>	<u>Concentration ppm, wet wt. (unless otherwise indicated)</u>	<u>Location</u>	<u>Reference</u>
Zinc	20-50	Denmark	Jorgensen and Pedersen, 1994
	2.36-3.8	Turkey	Kucuksezgin and Balci, 1994
	1.1-10.7	Pakistan	Tariq et al., 1991

References cited above:

Altar, K.M. et al. 1992. Levels of arsenic in fish from the Arabian Gulf. *Marine Pollution Bulletin* (G.B.) 24:94.

Barghigiani, C. and S. deRamien. 1992. Mercury content in different size classes of important edible species of the Northern Tyrrhenian Sea. *Marine Pollution Bulletin* (G.B.) 24:114.

Hornung, H. et al. 1994. Distribution and composition of fatty acids in muscle lipids of inshore fish and deep water sharks from the Eastern Mediterranean. *Marine Pollution Bulletin* (G.B.) 28:448.

Jorgensen, L.A. and B. Petersen. 1994. Trace metals in fish used for time trend analysis and as environmental indicators. *Marine Pollution Bulletin* (G.B.) 38:169.

Kucuksezgin, E. and A. Balci. 1994. Heavy metal concentrations in selected organisms in Izmir Bay, Turkey. *Marine Pollution Bulletin* (G.B.) 28:333.

Pastor, A. et al. 1994. Levels of heavy metals in some marine organisms from Western Mediterranean area (Spain). *Marine Pollution Bulletin* (G.B.) 28:50.

Tariq, J. et al. 1991. Concentration correlations between major cations and heavy metals in fish from the Arabian Sea. *Marine Pollution Bulletin* (G.B.) 22:562.

Conclusions Regarding Mercury

Average edible fish tissues concentrations were well below the 0.500 ppm Hawaii Department of Health, Services Action Level. (See Table G-3-14 for listing of action levels.) When compared to other areas, the Honouliuli soldierfish have typical concentrations of mercury in their muscle tissue (Table G-3-6), with one exception. This is a value of 1.28 found in a 1994 composite. This level exceeds the FDA Action level but appears to be an anomalous value which cannot be explained.

Table G-3-6. Muscle Tissue Mercury Levels in Composite Samples of Rig-Caught Fish, 1991-1995 Honouliuli Outfall Diffuser Region Analyte concentration in mg/kg wet weight

<u>Species</u>	<u>Year</u>				
	<u>1991</u>	<u>1992</u>	<u>1993</u>	<u>1994</u>	<u>1995</u>
Menpachi	0.13	0.08	0.026	0.059	0.11
Ta'ape	0.06	0.02	0.008	0.078	0.16
Akule	0.09	0.10	0.034	1.28	0.45

There is no bioaccumulation of mercury of public health significance now evident near the Honouliuli outfall that can be attributed to the wastewater discharge. There has been no increase in sediment concentrations of mercury near the outfall. There does not appear to be any association between sediment concentrations of mercury and tissue burdens in fish.

Arsenic

Arsenic is a common semivolatile trace element, well known for its toxic effects on humans when dosed in small amounts in its purest forms. It occurs naturally in seawater in various forms. In organisms, it is detoxified via production of organic forms of arsenic which are less toxic and more readily excreted.

Arsenic is of interest because it is known to be naturally high in sediments in the marine environment. While high arsenic levels can often be found, it is important to note that only the inorganic fractions of available arsenic are of health concern. The inorganic portion is often less than 10 percent of the total arsenic reported in analyses. Using total arsenic values can contribute to a high percentage of the risk of cancer when used in a standard human risk assessment model incorporating fish consumption (CSDOC, 1993). Thus, any modeling efforts must be adjusted to account for the organic fraction which requires a different analysis.

Arsenic levels in the muscle tissue of fish caught off the Honouliuli outfall appear to be within the range of values previously reported for the Hawaiian Islands. Levels of arsenic in muscle tissue from fish caught off Honouliuli range from 0.40 to 5.07 ppm in big-eyed scad,

1.1 to 8.1 ppm in blue-lined snapper, and 5.9 to 15.5 ppm in golden-finned squirrelfish (Table G-3-7). Figure G-3-1 shows average concentrations of arsenic for the various fish species analyzed. The data presented show that the concentrations have varied significantly over time and do not appear to show any overall pattern. Given the infrequency of sampling and fact that the fish are highly mobile, one would not expect that levels would show any pattern.

Table G-3-7
Muscle Tissue Arsenic Levels in Composite Samples of Rig-Caught Fish, 1991-1995
Honouliuli Outfall Diffuser Region
Analyte concentration in mg/kg wet weight

<u>Species</u>	<u>Year</u>				
	<u>1991</u>	<u>1992</u>	<u>1993</u>	<u>1994</u>	<u>1995</u>
Menpachi	5.9	11.8	8.1	8.74	15.5
Ta'ape	3.3	4.49	1.1	5.96	8.1
Akule	1.68	5.07	8.1	3.74	0.4

Sand Island data for the years 1991 through 1993 are available for comparison for ta'ape and akule (Brock, 1994). Values for arsenic in muscle tissue in fish caught at the Sand Island diffuser ranged from 3.14 to 16.5 mg/kg in ta'ape and 1.64 to 3.55 mg/kg in akule.

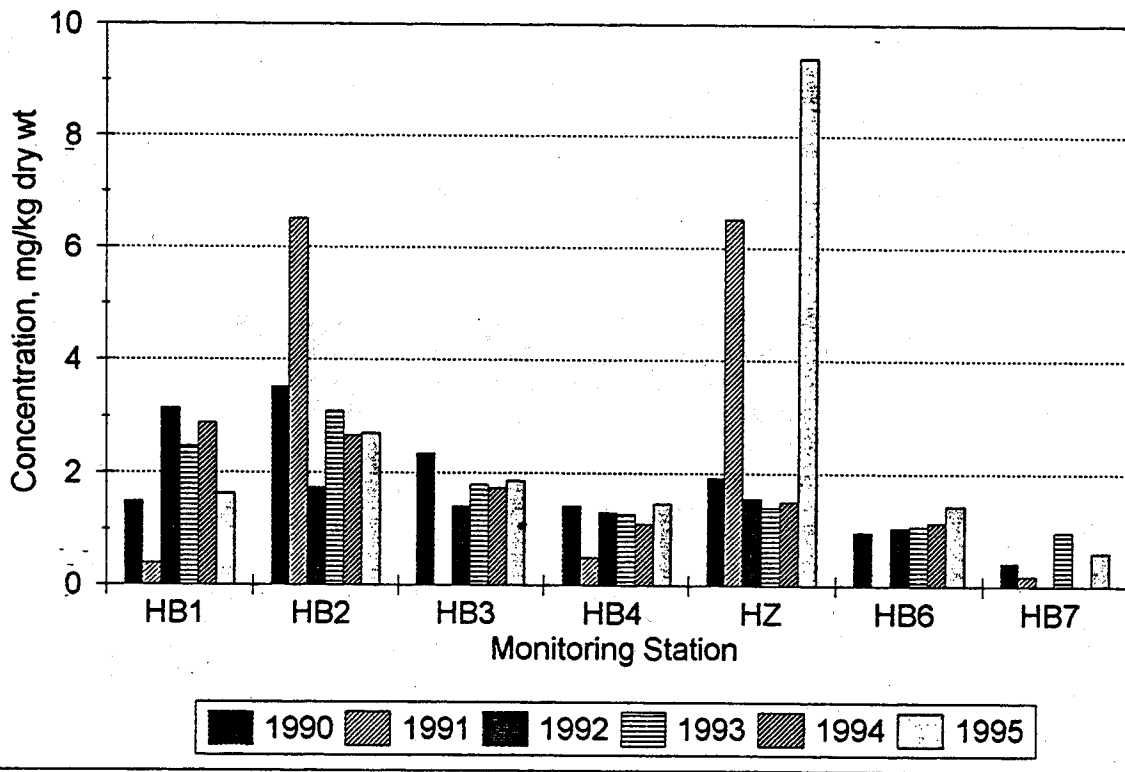
The relationships and factors influencing uptake, metabolism, excretion and bioaccumulation of arsenic in fish are not well known. Mearns et al. (1991) in a comprehensive evaluation of arsenic in fish tissues in Southern California suggested that there is no correspondence between arsenic in sediments and arsenic levels in the tissues of animals. The large data set for fish tissues collected near the city of San Diego's Point Loma outfall confirm this (Tetra Tech, 1995). These large data bases have shown that there is a wide fluctuation in arsenic levels in fish over time. These fluctuations occurred while the arsenic contributions from wastewater discharges were decreasing.

Evaluation of sediment levels indicated no apparent association between muscle tissue burdens and sediment levels. The same conclusion can be drawn for the Honouliuli outfall. Effluent concentrations are below detection limits (<2 to <10 mg/l) while sediment arsenic levels range from <0.4 to 9.7 mg/l. (See Attachment C-3 of Appendix C for details.) Fish tissue burdens show no significant increase over sediment levels, indicating that bioaccumulation is not occurring.

Cadmium

Cadmium is a common trace element widely used in electroplating, in paints as a pigment, in batteries and as a plastic stabilizer. It has not been found at notable concentrations in the Barbers Point influent or effluent and has not been one of the targets of source-control efforts in the City & County of Honolulu's pretreatment program to date. Levels in effluent

Sediment Arsenic Concentrations Annual Averages by Station



Harding Lawson Associates
Engineering and
Environmental Services

Sediment Arsenic Concentrations
Honouliuli Wastewater Treatment Plant
Ewa Beach, Oahu, Hawaii

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have been in the range of <2 to <5 ppb, below detection. Sediment levels have ranged from below detection limits (<0.005 to 17 ppm) (Figure G-3-2).

There was only a single reportable composite of muscle tissue containing cadmium. This was for muscle tissue from big-eyed scad in 1993 at a very low concentration of 0.004 ppm (Table G-3-4). This concentration is about the level of detection in sediments and indicates no bioaccumulation above environmental levels.

Chromium

Chromium, like cadmium, is a common trace element widely used in industrial applications and has not been a target of source control efforts of the metal plating and hide tanning industries in the City & County of Honolulu's pretreatment program. Effluent levels ranged from <7 to 50 µg/l (ppb). Sediment levels have ranged from 5.9-23.8 ppm, dry weight (Figure G-3-3).

These values appear to be typical of Mamala Bay sediments.

Chromium levels in muscle, as presented in Table G-3.8, are limited to a few samples all less or equal to than 0.1 ppm. These values are quite low compared to values measured worldwide.

Table G-3-8. Muscle Tissue Chromium Levels in Composite Samples of Rig-Caught Fish, 1991-1995 Honouliuli Outfall Diffuser Region Analyte concentration in mg/kg wet weight

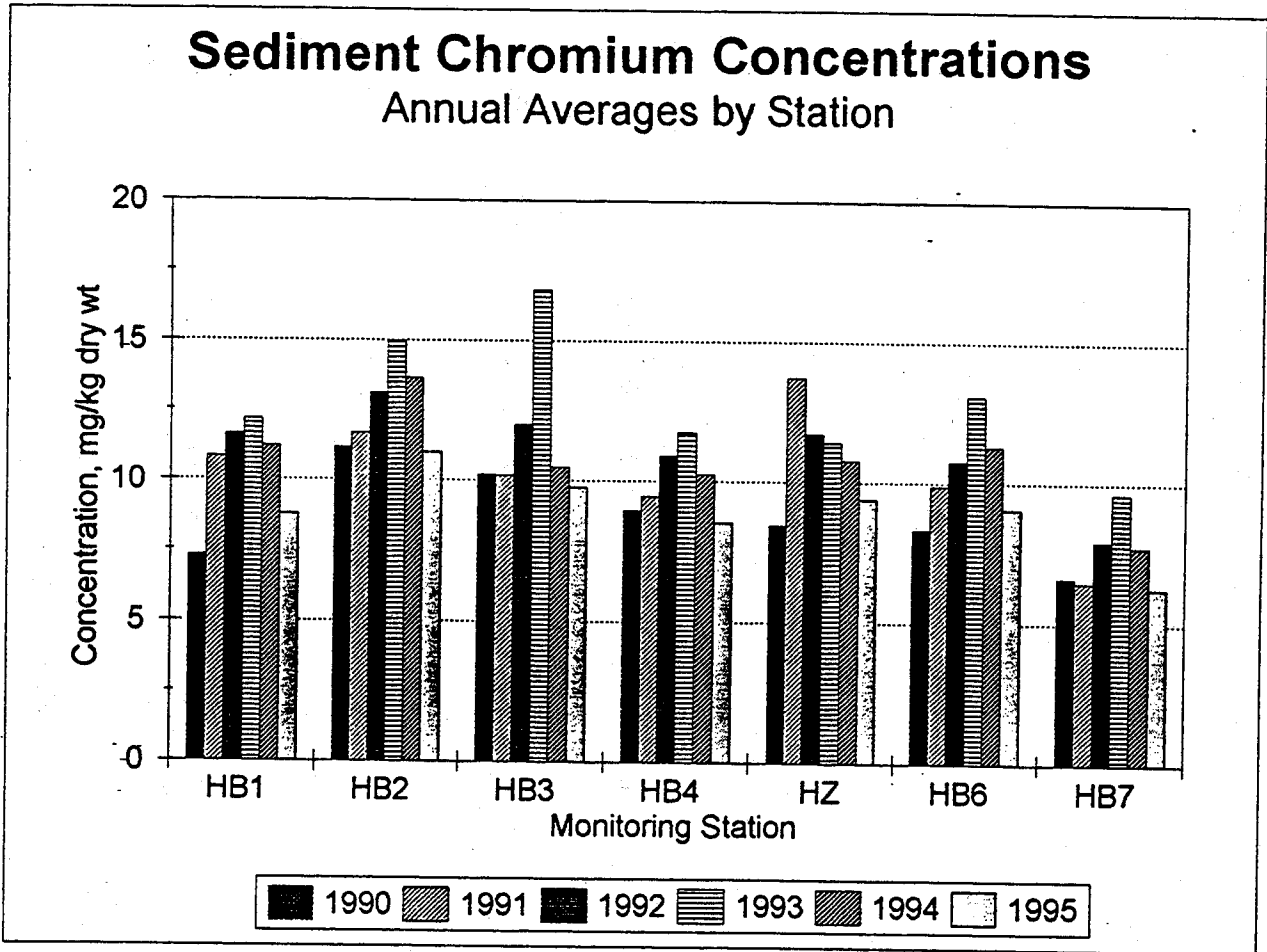
<u>Species</u>	<u>Year</u>				
	<u>1991</u>	<u>1992</u>	<u>1993</u>	<u>1994</u>	<u>1995</u>
Menpachi	BDL	BDL	0.07	ND<0.20	0.1
Ta'ape	BDL	BDL	0.09	ND<0.20	0.1
Akule	ND	0.02J	0.09	ND<0.2	0.1

Data show that chromium is not being bioaccumulated in fish where sediment levels are high, and certainly there is no evidence of bioaccumulation near the Honouliuli diffuser.

Copper

Copper is the metal with the highest concentration in the Honouliuli effluent due to its widespread use in industrial, commercial and household products and applications. It is present in all types of wastes and materials in sewage, and can be leached from copper pipes. Copper, like other metals, has undergone a reduction as a result of source-control efforts in the Honouliuli pretreatment program (see Appendix H). Effluent levels now range between 26 and 70 µg/l (ppb). Sediment levels have ranged from 8.5 to 25 ppm

Sediment Chromium Concentrations Annual Averages by Station



Harding Lawson Associates
Engineering and
Environmental Services

Sediment Chromium Concentrations
Honouliuli Wastewater Treatment Plant
Ewa Beach, Oahu, Hawaii

FIGURE

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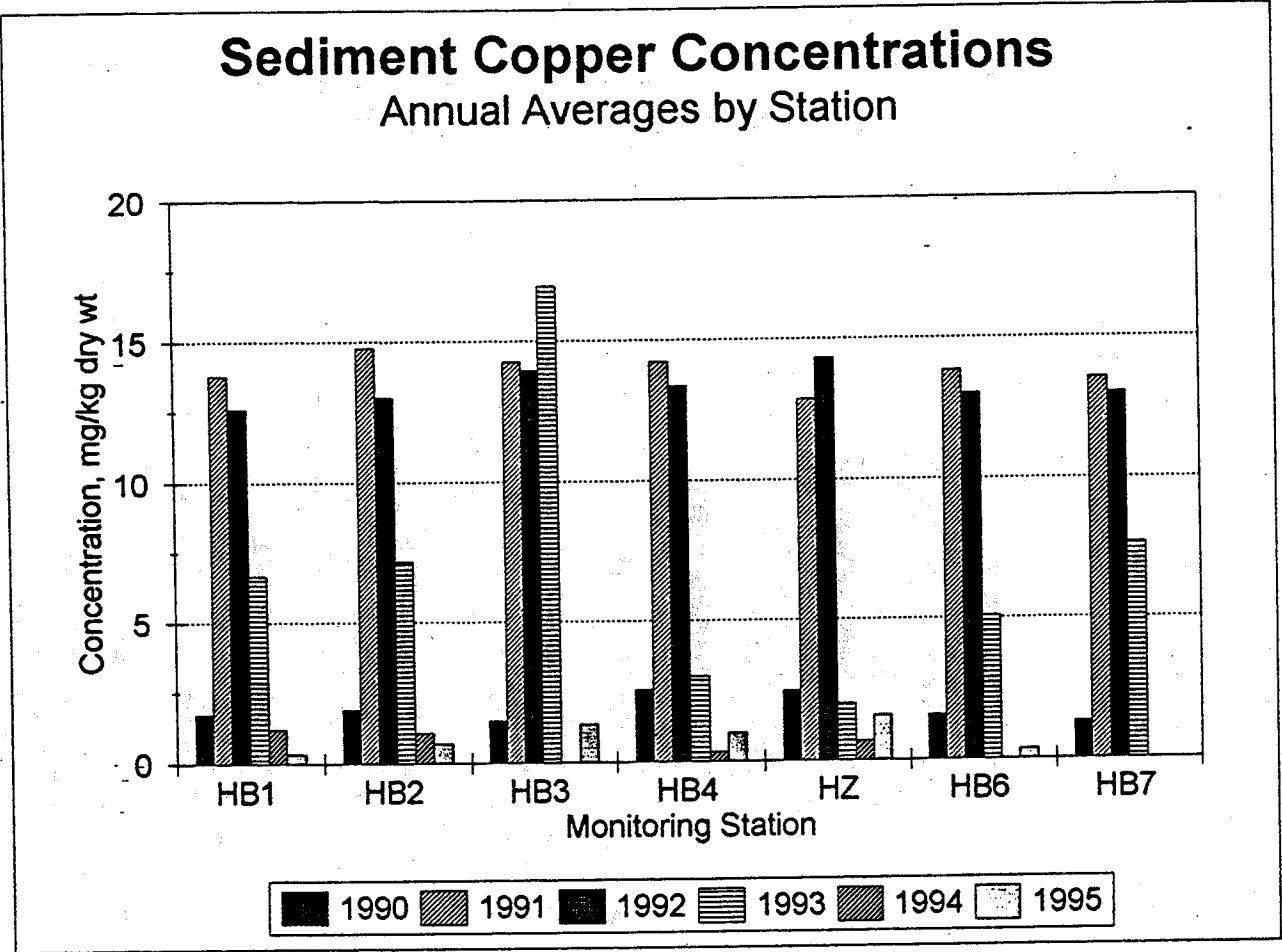
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Sediment Copper Concentrations Annual Averages by Station



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Sediment Copper Concentrations
Honouliuli Wastewater Treatment Plant
Ewa Beach, Oahu, Hawaii

G-3-3

(Figure G-3-4). The ZID area of the Honouliuli outfall has concentrations averaging between 1.0 to 14.3 ppm on a yearly basis.

A summary of copper levels measured in the three fish species studied near the Honouliuli outfall is presented in Table G-3-9. Copper in the muscle tissue of composite of akule had the highest recorded value of 1.2 ppm in 1993. Otherwise, the values were very similar in all species. Overall, the tissue burden values for all three species ranged from below detection limits (<0.10 ppm) to the high of 1.2 ppm.

Table G-3-9. Muscle Tissue Copper Levels In Composite Samples of Rig-Caught Fish, 1991-1995 Honouliuli Outfall Diffuser Region Analyte concentration in mg/kg wet weight

<u>Species</u>	<u>Year</u>				
	<u>1991</u>	<u>1992</u>	<u>1993</u>	<u>1994</u>	<u>1995</u>
Menpachi-	0.18	0.10	ND	0.2	0.7
Ta'ape	0.25	0.37	ND	0.3	0.3
Akule	0.29	0.13	1.2	0.2	0.65

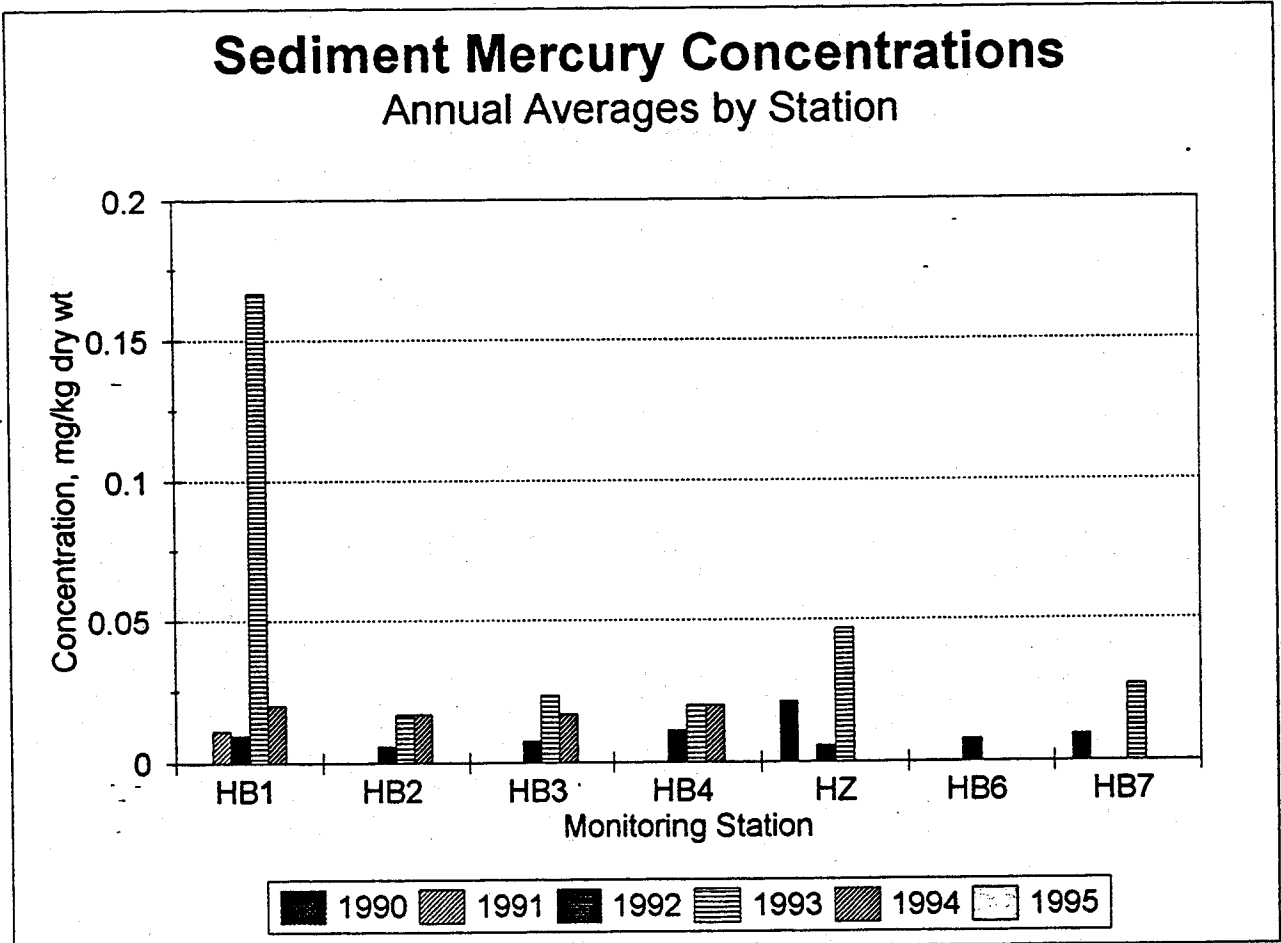
The only available data for comparing copper levels in the various species caught off Honouliuli is the data for Sand Island where levels ranged from 0.18 to 1.3 mg/kg for ta'ape and 0.49 to 3.36 mg/kg for akule (Brock, 1994). No values for menpachi are available from Sand Island monitoring. Fish from California were reported to have copper muscle tissue levels (off Orange County and in Santa Monica Bay) ranging from 0.096 to 0.21 ppm (MEC, 1992). Fish in Hawaii exceed these levels; however, the copper levels in the fish caught off Honouliuli appear to be similar to the range of values reported elsewhere in the world (Table G-3-5) which have ranged from 0.8 to 18 ppm. Given that sediment values of copper are up to an order or magnitude higher, there is no evidence of bioaccumulation.

Lead

Lead has been widely distributed in the environment largely as a result of its prior use as a gasoline additive and in paints. Both of these uses have been dramatically curtailed and lead levels today are decreasing. Lead in wastewater has its origin in various industrial uses and lead solder in water piping systems. Lead levels in wastewater have been declining over the years and are now below detection levels in the Honouliuli effluent (<100 µg/l).

Sediment levels have ranged from below detection limits to 2.0 ppm, dry weight with an average of about 1 ppm (Figure G-3-5). These values are quite low compared to values typical of the California mainland shelf where sediment mean values range from about 4.1 to 13 ppm in unpolluted areas along the 60-meter-depth contour (Mearns et al., 1991). Lead levels in sediments from the LA-5 dredge disposal site off San Diego have been measured at 163.4 ppm.

Sediment Mercury Concentrations Annual Averages by Station



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Sediment Mercury Concentrations
Honouliuli Wastewater Treatment Plant
Ewa Beach, Oahu, Hawaii

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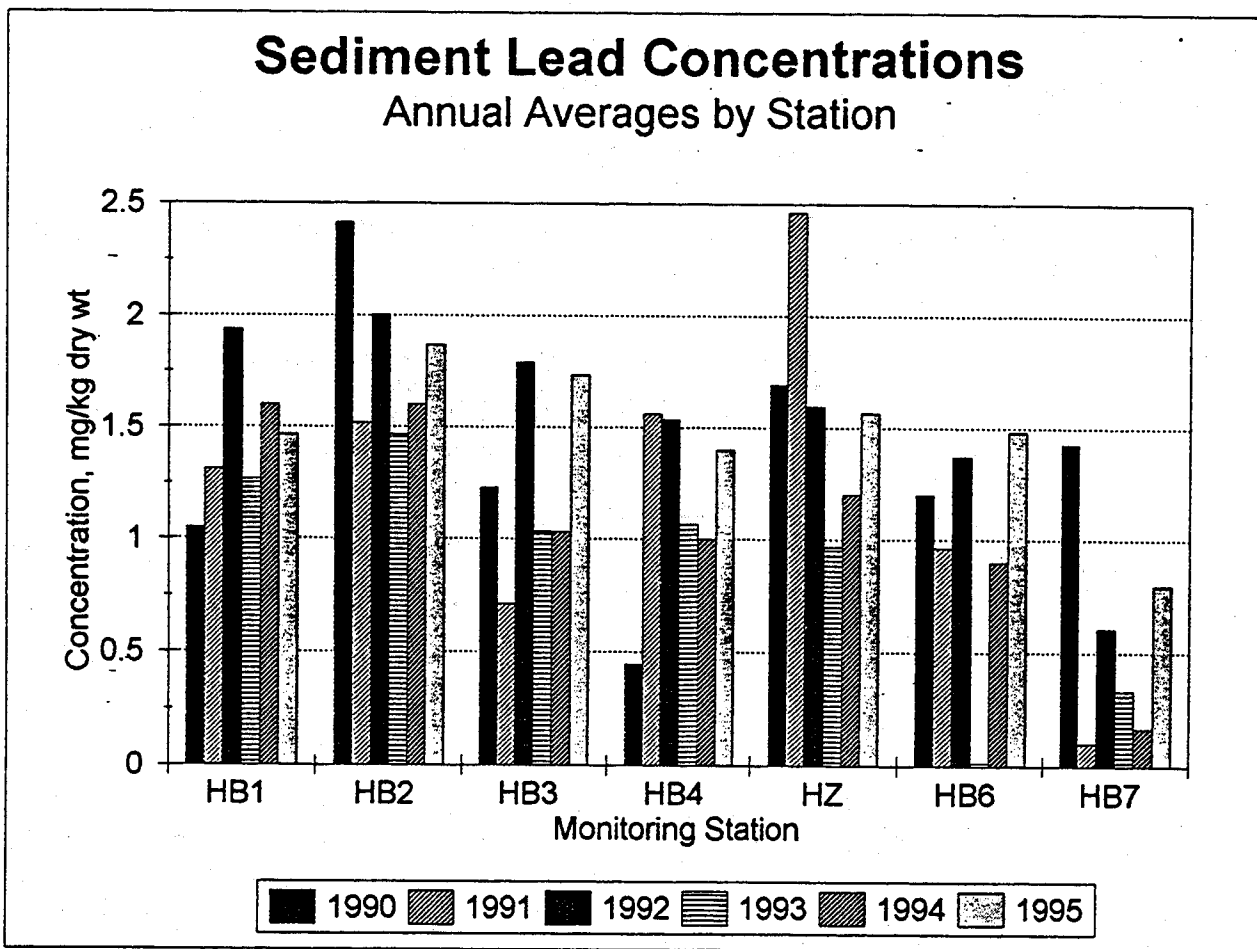
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Sediment Lead Concentrations Annual Averages by Station



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Sediment Lead Concentrations
Honouliuli Wastewater Treatment Plant
Ewa Beach, Oahu, Hawaii

FIGURE

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To date, none of the fish composite samples of muscle tissue from the Honouliuli area has shown detectable lead (Tables G-3-2 through G-3-4). Levels are all <0.1 ppm.

Nickel

Nickel has been used in industrial, commercial and household products and applications, and thus has a widespread distribution in the environment, including the marine environment of nearshore waters. Effluent levels in the Honouliuli effluent are very low (below detection limits ranging between 5 and 50 ppm). Sediment levels have ranged from <0.044 to 16.7 ppm with an average of <3 to 11 ppm in the vicinity of the outfall diffuser and an average ranging from <3 to 6 ppm at reference stations away from the outfall (Figure G-3-6).

These values are typical of the Mamala Bay sediment mean values and are very low compared to values measured in Southern California. Mearns et al. (1991) did not report on nickel in fish tissues due to a paucity of data.

The city's monitoring data show only two reportable nickel measurements in the muscle of fish caught near the Honouliuli outfall (Table G-3-11).

Table G-3-11. Muscle Tissue Nickel Levels in Composite Samples of Rig-Caught Fish, 1991-1995 Honouliuli Outfall Diffuser Region
Analyte concentration in mg/kg wet weight

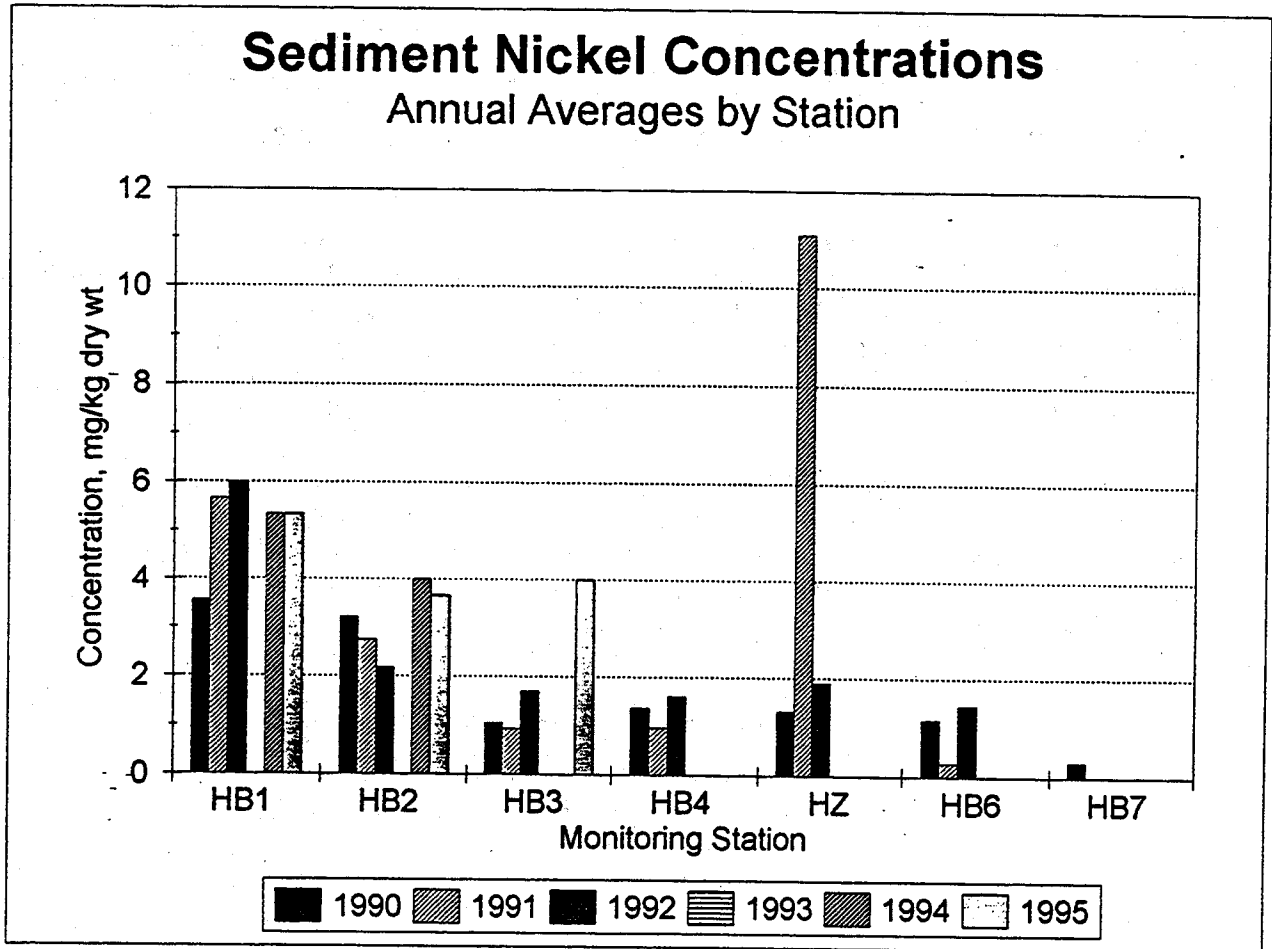
Species	Year				
	1991	1992	1993	1994	1995
Menpachi	BDL	BDL	BDL	ND<0.5	0.2
Ta'ape	BDL	BDL	BDL	ND<0.5	ND<0.5
Akule	0.06	BDL	BDL	ND<0.5	<0.20

A single composite of menpachi muscle in 1995 was found to have a concentration of 0.2 ppm, while a single composite muscle tissue in akule in 1991 had a level of 0.06 ppm (Table G-3-11). Data from the San Diego bioaccumulation monitoring studies indicate that muscle tissue is roughly equivalent to sediment levels and can be as much as two-fold higher, indicating no bioaccumulation is occurring (City of San Diego, 1995).

Selenium

Selenium has been widely distributed in the environment because it is a natural element with a diversity of uses, particularly in agriculture and industry. Another use which contributes to the concentrations found in wastewater is in dandruff shampoos. Selenium levels in wastewater have only been measured in recent years and generally averaged <2 µg/l with a maximum concentration of <3 µg/l (below detection limits).

Sediment Nickel Concentrations Annual Averages by Station



FIGURE



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Sediment Nickel Concentrations
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Selenium levels in the muscle of fish caught off Honouliuli have been limited. Composites of akule muscle were found to have a concentration ranging from 0.45 to 0.6 ppm (Table G-3-4) while ta'ape had muscle tissue levels ranging from 0.285 to 0.6 ppm (Table G-3-3). Measurable quantities of selenium in concentrations ranging from 0.4 to 0.42 ppm (Table G-3-2) were found in menpachi composite samples.

Silver

Silver is largely present in wastewater as a result of its use in photography. It is not a compound normally found in marine animal tissues and has been shown to be a useful indicator of the presence of an outfall discharge in the various Mussel Watch Programs (NOAA, 1989). Levels of silver in the Honouliuli effluent are generally measured to be below detection limits <10 to <20 µg/l.

Sediment levels have mostly been reported to be below detection limits with a maximum of 8.4 ppm (at Station HB1, a reference station) with a wide average inter-annually (0.05 to 8.0 ppm) (Figure G-3-7). Typical values reported for sediments near outfalls in the Southern California Bight are in the range of 0.24 to 8.9 ppm with sediment means ranging from 0.75 to 1.2 ppm in various historic surveys of sediment quality off Point Loma in San Diego (with an overall range of 0.37 to 1.7 ppm) in the past (Mearns et al., 1991).

Silver levels in the muscle of fish caught off Point Loma in San Diego were below reportable levels (5 x detection limit). Silver levels in muscle composites from all three Hawaiian species have been measured at very low levels ranging from 0.034 to 0.05 ppm with similar concentrations averaging about 0.04 ppm for all three species (Table G-3-12). Such values are typical for the levels from fish caught worldwide (Table G-3-5).

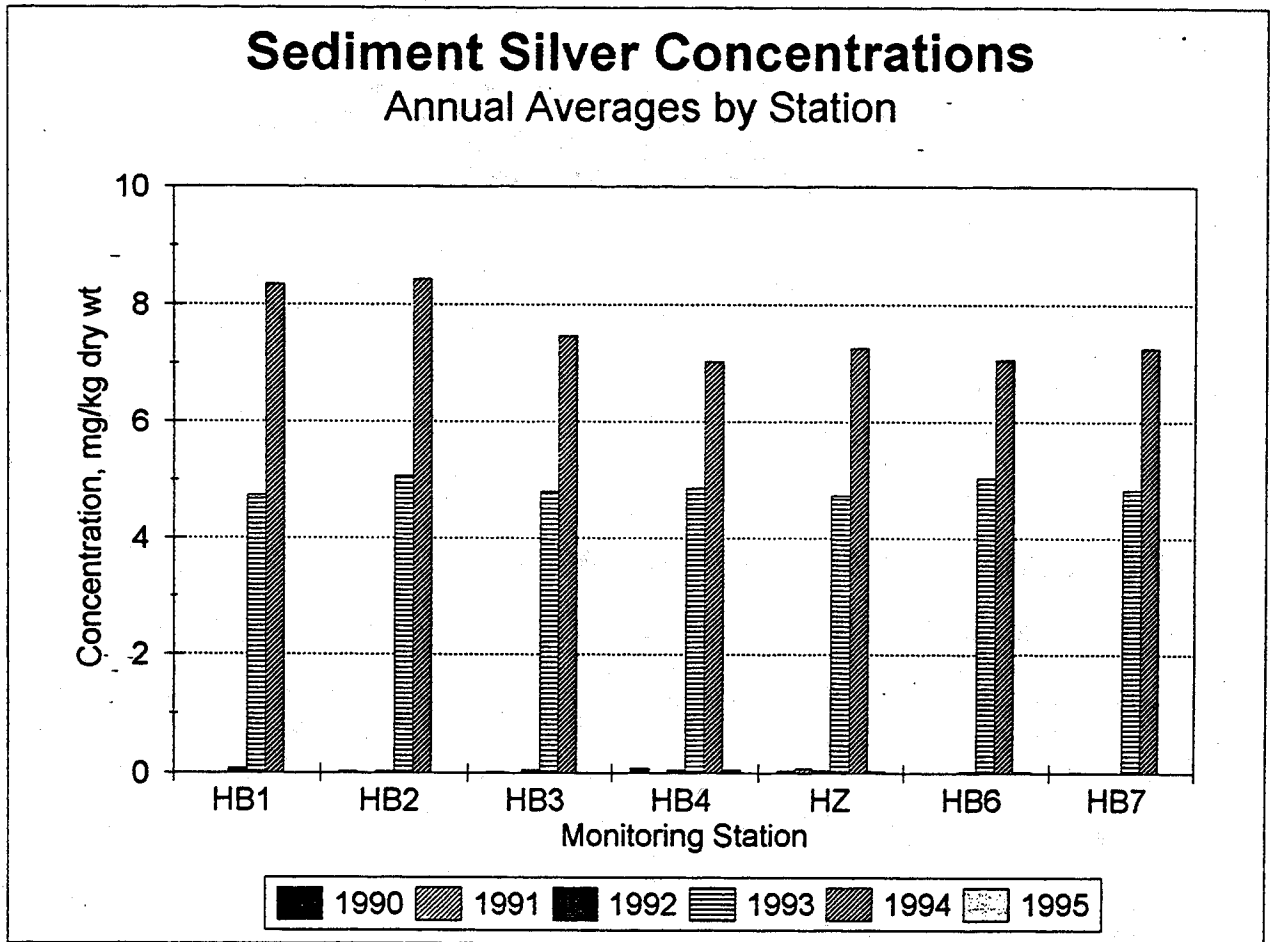
Table G-3-12. Muscle Tissue Silver Levels in Composite Samples of Rig-Caught Fish, 1991-1995 Honouliuli Outfall Diffuser Region Analyte concentration in mg/kg wet weight

Species	Year				
	1991	1992	1993	1994	1995
Menpachi	NR	<2.99	0.05	0.034	ND<0.02
Ta'ape	BDL	<3.38	BDL	0.042	ND<0.02
Akule	BDL	<2.84	0.04	ND<0.20	ND<0.20

Zinc

Zinc is the metal with the highest measurable concentrations in the Honouliuli effluent. Zinc is found in batteries and vehicle tires, and its widespread use in industrial, commercial and household products and applications makes it ubiquitous in the environment. To date, zinc has not been a target of source control efforts in the city's pretreatment program (see Appendix H). Effluent levels have ranged from 60 to 160 µg/l (ppb). Sediment levels have ranged from <1.9 to 14 ppm, with an average of about 5 ppm at the ZID station HZ

Sediment Silver Concentrations Annual Averages by Station



FIGURE



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Ewa Beach, Oahu, Hawaii

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(Figure G-3-8). These values are much lower than typical fine-grained sediment levels found in the Southern California Bight, where mean values range from about 40 to 72 ppm in areas remote from wastewater discharges (60 meter depth) to as high as 400 to 500 ppm in contaminated areas of San Diego Harbor (Mearns et al., 1991).

Reportable concentrations of zinc in composite fish muscle samples from the Honouliuli outfall diffuser region show a relatively narrow range of values ranging from 1.7 to 5.8 ppm in akule, which showed the greatest variation in concentration. The two other species showed a very narrow range (2.1 to 3.2 ppm in menpachi and 2.3 to 3.66 in ta'ape). These levels are very low compared to fish caught in Southern California 3 to 65 ppm (City of San Diego, 1995). The fluctuation of zinc muscle tissue levels over time for the three species is shown on Figure G-3-14.

Table G-3-13. Muscle Tissue Zinc Levels in Composite Samples of Rig-Caught Fish, 1991-1995 Honouliuli Outfall Diffuser Region Analyte concentration in mg/kg wet weight

Species	Year				
	1991	1992	1993	1994	1995
Menpachi	2.75	2.25	2.1	3.2	2.8
Ta'ape	2.31	3.66	2.3	2.4	3.4
Akule	3.67	2.03	5.8	1.7	4.95

Bioaccumulation of Chlorinated Hydrocarbons

There are two chlorinated hydrocarbons which are generally the focus of most bioaccumulation studies. These are the PCBs (various Aroclor mixtures) and total DDT (DDT and the derivatives and breakdown products DDE and DDD). Effluent measurements show that they are consistently found below detection limits most of the time. On one recent occasion a detectable level of 4,4'-DDD was found (0.13 $\mu\text{m/l}$ in 1994) in a single specimen.

Chlorinated Hydrocarbons in Sediments

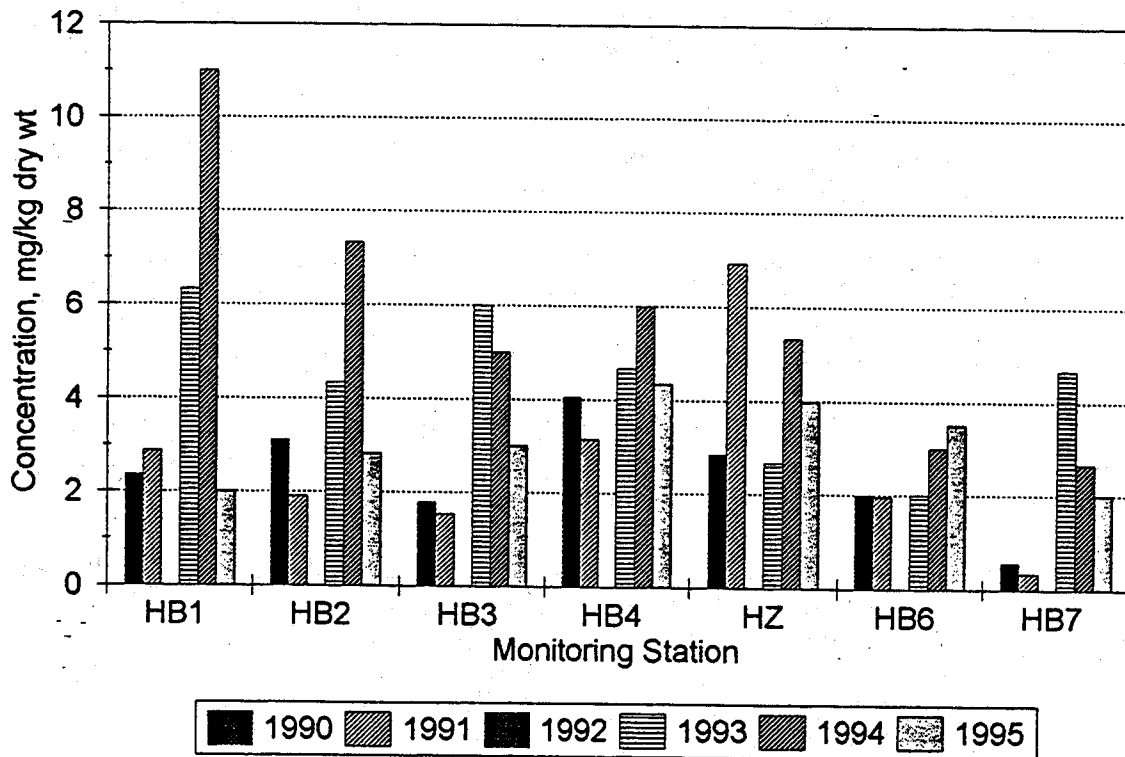
Total DDT is routinely detected in sediments at low concentrations, while PCBs are not. Levels of these two constituents in sediments are discussed in more detail in Appendix C, Attachment 3.

There is no discernible discharge-related trend associated with DDT in sediments.

Chlorinated Hydrocarbons in Fish Tissue

Overall, the concentrations of DDT and its derivatives in fish muscle tissue are generally below detection limits of <0.002 ppm (Tables G-3-2 through G-3-4). The highest reported value was for a menpachi composite in 1991 which contained 0.018 ppm of total DDT. All muscle tissue samples were well below the U.S. Food and Drug Administration level of

Sediment Zinc Concentrations Annual Averages by Station



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Sediment Zinc Concentrations
Honouliuli Wastewater Treatment Plant
Ewa Beach, Oahu, Hawaii

FIGURE

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5.0 ppm. Concentrations in the muscle tissues of various composite samples for the various species averaged from 0.005 to 0.018 ppm and were well below the NAS wildlife protection conservative criterion of 0.05 ppm established for a composite (whole body) of 30 or more fish (see Table G-3-14).

Other Measurable Priority Pollutants

Interpretation of Results

Interpretation of the analytical results of the levels of contaminants found in the tissues of fish has been done in accordance with applicable methods. Interpretation is generally limited to comparisons and calculations of risk based on local consumption patterns and use of available EPA risk assessment models borrowed from the Superfund Program. Given the limited data base, such interpretations are of limited value and are made difficult by a variety of factors including the following:

- Comparisons are limited by species-specific differences, as well as by differences in sex, age, and reproductive maturity within a species.
- The contaminant burdens found may be derived from a variety of sources and may not reflect local sediment levels or water quality conditions. Prey species and the ability of the prey to accumulate contaminants are key factors. Without a consistent pattern, it is difficult to determine the origin of contaminants.

The City & County of Honolulu's fish bioaccumulation data collection efforts, like that of other dischargers in the 301(h) program are subject to the difficulties of attempting to find suitable reference data for comparative purposes.

There are no specific national or state criteria for evaluating fish health, assuming pathological conditions, or contaminant burdens. There are some longstanding criteria for the assessment of consumption quality for humans or for wildlife from a variety of agencies (National Academy of Sciences, 1973; U.S. Food and Drug Administration, 1985; and Office of Environmental Health Hazard Assessment of the California Department of Health Services, 1991). These criteria can be used for general purposes in evaluating the possible health and ecological significance of the measured tissue burdens. A summary of these criteria is shown in Table G-3-14.

Table G-3-14. Bioaccumulation Criteria Relevant to Impact Assessment Levels in Marine Organisms (ppm)

<u>Chemical</u>	<u>NAS Recommended Guideline (whole fish)</u>	<u>FDA Action Level or Tolerance (edible portion)</u>	<u>OEHHA Trigger or Health Advisory Level (edible portion)</u>
	<u>(A)</u>	<u>(B)</u>	<u>(C)</u>
Total PCB	0.50	2.0*	0.100
Total DDT	0.05	5.0	0.100
Aldrin	(D)	0.030*(E)	—
Dieldrin	(D)	0.30*(E)	—
Heptachlor	(D)	0.30*(E)	—
Heptachlor epoxide		0.30*(E)	—
Lindane	0.050	—	—
Chlordane	0.050	0.30	0.023
Endosulfan	0.050	—	—
Methoxychlor	0.050	—	—
Mirex	0.050	—	—
Toxaphene	0.050	5.0	—
Hexachlorobenzene	0.050	—	—
Any other chlorinated hydrocarbon pesticide	0.050	—	—
Mercury	—	1.0* (as methyl mercury)	0.50 (as total mercury)

*Fish and shellfish.

- A. National Academy of Science. 1973. *Water quality criteria*, 1972 (Blue Book). The recommendation applies to any sample consisting of a homogeneity of 25 or more fish of any species that is consumed by fish-eating birds and mammals, within the same size range as the fish consumed by any bird or mammal. No NAS recommended guidelines exist for marine shellfish.
- B. U.S. Food and Drug Administration. 1984. *Shellfish sanitation interpretation: action levels for chemical and poisonous substances*. A tolerance, rather than an action level, has been established for PCB.
- C. Office of Environmental Health Hazard Assessment. 1991. *A study of chemical contamination of marine fish from Southern California. II. Comprehensive study*. A health advisory level, rather than a trigger level, has been established for mercury. These values should only be used if they specifically apply to the water bodies for which they were developed.
- D. Limit is 5 ppm wet weight. Singly or in combination with other substances noted by footnote D.
- E. Singly or in combination for shellfish.

The presence of potentially carcinogenic, mutagenic, or acutely toxic chemicals in fish and shellfish tissue is commonly accepted as proof of bioaccumulation which could eventually adversely affect human health. Potential for bioaccumulation is a criterion commonly applied in developing water quality criteria used for establishing and evaluating permit limits for waste discharges to the marine environment. Concern about bioaccumulation is fueled by well-publicized harmful effects such as the effect of DDT on eggshells of predatory birds and the effect of mercury on humans (Minamata disease) who have consumed contaminated fish. Human health criteria have been promulgated and adopted by the Hawaii Department of Health.

Review of a portion of the growing body of scientific literature, however, suggests that caution is needed in discussing bioaccumulation of contaminants. Although there are clearly effects in nature that are attributable to bioaccumulation of contaminants, there are also many assumptions about harmful effects that do not withstand rigorous analysis. Some of the factors influencing bioaccumulation are elimination and detoxification.

Elimination

Bioconcentration and bioaccumulation alone are not useful measures for assessing risk to biological communities or human health. Many chemicals undergo some degree of bioconcentration and bioaccumulation; but when organisms are transferred to a clean environment, many of these chemicals are rapidly excreted. Thus, persistence is a factor that must be considered in species with wide-ranging movements (such as many fish).

Both the toxicity and the bioaccumulation potential of a toxic compound are greatly affected by the rate of elimination from the organism. Common processes by which organisms can cleanse themselves of contaminants include excretion, defecation, diffusion, body secretions (e.g., mucus), and molting (in the case of crustaceans) (Bryan, 1979). In most cases, cleansing (depuration) implies that the organism is exposed to reduced external levels of contamination. There is evidence, however, that some marine organisms are capable of regulating tissue levels of certain metals while still in contaminated environments; i.e., concentrations in the tissues are less than what would be expected based on external concentration. Polychaetes, decapod crustaceans, and fish show some evidence of regulation of levels of metals in the tissues, whereas bivalve mollusks do not (Bryan, 1979).

Detoxification

Most animals have means of protecting themselves from naturally occurring toxics. One way is through a group of proteins of the metallothionein type which binds metals, thereby making the metals nontoxic and biologically unavailable (Brown et al., 1985). These proteins normally occur at relatively low levels in tissues, and synthesis is induced by exposure to contamination by metals (Bryan, 1979). Research on the detoxification process suggests that metallothioneins are effective detoxification mechanisms for metals unless the metal levels in the environment (and therefore the organism) are so high or increase so rapidly as to exceed the body's capacity to manufacture and store these proteins.

One good example is arsenic, a very ubiquitous compound in marine organisms (Bryan, 1979). The data compiled suggest that arsenic in marine organisms primarily (80 to 90

percent) occurs in a less toxic organic state, which is more readily excreted than arsenite and less toxic. Most groups of marine organisms appear to be able to synthesize these organic arsenic compounds. Thus, the body burdens normally measured (total arsenic) may not reflect any relative degree of potential effects on physiology or hazard to human health from consumption. Measurement of total arsenic is not reflective of the contaminant level of concern, because it is the elemental arsenic which poses a toxic threat if contaminated tissues are consumed by humans.

Risk Assessment

The risks associated with the consumption of fish contaminated with various potentially toxic pollutants can be assessed using various methods ranging from comparisons of concentration to full risk assessments using cumulative risks over 70 years.

Public health risk assessments were undertaken by M&E Pacific for the city in 1989 as part of the water quality studies for the Honouliuli outfall (M&E Pacific, 1989). The studies were based on those toxics found in wastewater effluents discharged to the marine environment. The only two constituents consistently found above detection limits were the two trace metals, copper and zinc. These two constituents were also found in fish tissue samples collected as part of the bioaccumulations studies provision of the 301(h) modified NPDES Permit. These two particular metals are almost universally found in the marine environment in sediments and tissues of marine organisms.

Zinc is not considered to be a hazard in marine waters under normal circumstances. Copper can be a hazard at high dosages, but is also an essential nutrient at low concentrations.

Risk assessment analyses are based on evaluation of the dosage to which a person might be exposed and comparing this dosage to the permissible limit, which is defined in terms of the average daily intake (ADI). Fish tissue from specimens collected from both the Honouliuli and Sand Island diffuser stations by hook-and-line were analyzed, and the results used to calculate a dosage of copper from consuming 165 grams (5.3 ounces, or about 0.33 pounds) per day of seafood (daily consumption) for a lifetime of 70 years. The results showed a dose of 14 percent of the ADI. No hazard is expected at this dosage.

This finding concurs with the original 1972 Water Quality Program for Oahu recommendation of pretreatment/source control for the elimination toxics in the city's collection system. That recommendation formed the basis for the current ongoing pretreatment program approved by EPA.

In contrast to the outfall risk assessment's low hazard potential, crab tissue from specimens collected from Pearl Harbor would give a dose of 119 percent of ADI, which is a cause for concern. The same tissue samples also showed presence of 4-4' DDT. It is noteworthy that Pearl Harbor has been placed on the National Priority List as a designated Superfund site that must undergo remediation to lower the levels of contaminants found in the terrestrial and water environments in and around the harbor and base.

The high levels of contaminants found in the crab tissue sample are not related to the Mamala Bay outfall discharges. Instead, nonpoint source contamination exerts a greater degree of influence.

Conclusions

Contaminant concentrations measured in the muscle tissues of fish collected during this program were below the respective FDA action levels (for total PCBs, total DDT+, and mercury). However, FDA action levels have been established only for nine contaminants (seven pesticides, mercury, and PCBs) and, with the exception of mercury, were intended to regulate interstate commerce of consumable products and not to protect the health of fish or to govern human consumption of seafood.

From the data collected to date, there is no evidence that the outfall discharge is contributing to the bioaccumulation of contaminants in fish.

The concentrations of most contaminants were low. For most constituents other than a few trace metals, the levels are routinely below detectable levels. This is the case for DDT and derivatives and PCBs.